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(54) Title: SENSOR WITH HOLOGRAPHIC MULTIPLEXED IMAGE DISPLAY

(57) Abstract: A holographic sensor comprising a thin film polymer matrix that undergoes a change in response to a substance to be sensed, the matrix containing within its volume a set of two or more holographic recordings, each recording providing a holographic image when the sensor is illuminated, wherein the presence or appearance of each image is visible to the eye as a function of the response of the sensor to the substance to be sensed. The images provide the dynamic range of the sensor. Such a sensor can be used to provide a visible image that changes or appears to the eye in response to an analyte.

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SENSOR WITH HOLOGRAPHIC MULTIPLEXED IMAGE DISPLAY

Field of the Invention

The present invention relates generally to sensors and more particularly to a holographic multiplexed image sensor.

5 Background of the Invention

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Chemical sensors and biosensors in the form of volume holograms made in specially made polymer layers are known. WO-A-95/26499 discloses a sensor which comprises a reflection hologram made in a thin film of polymeric material where the polymer interacts with a substance to be detected so as to alter the optical properties of the hologram, thereby providing a means for detecting or quantifying that substance. More generally, this reference and also WO-A-99/64308 disclose the concept of a volume hologram sensor which provides a measurable or observable optical change.

Within the art of holography, multiple holographic images and methods for creating them in a single holographic recording material are known. US-A-4509818 discloses a method of making a three-dimensional holographic multiplexed image from a series of two-dimensional images. US-A-5103325 discloses a method of holographically recording a series of two-dimensional images such that the viewed holographic images are observed separately and distinctly from each other. US-A-5734485 discloses a method of producing three-dimensional still or moving scene holograms including recordings of computer-generated scenes.

These known systems produce sets of holographic images which are multiplexed in a degree-of-freedom which is only spatial, where the images are intended to be viewable by an observer as an artificially-produced three-dimensional image or as a set of images separated in space over a corresponding set of angles of view. The optical properties of the material in which these holograms are made are intended to be invariant in time and they are not intended to be altered chemically when functioning normally.

Summary of the Invention

An object behind the present invention is to provide a volume hologram sensor which provides a multiplicity of holographic images, where the set of images is multiplexed in the degree-of-freedom which is the dynamic detection range of the sensor, where each image, when visible, represents a finite region of the dynamic detection range.

According to a first aspect of the present invention, a holographic sensor comprises one or more films each containing within its volume a set of two or more

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holographic recordings, each recording providing a reflected holographic image when the sensor is illuminated by light and where each image is visible to the eye as an indicator that the sensor is showing a response to a predetermined range of concentration of a substance or group of substances to be sensed. More particularly, the presence or appearance of each image is visible to the eye as a function of the response of the sensor to a substance to be sensed; that response may involve the appearance or disappearance, or a change in, a visible image.

Typically, each image in the set of images has a reflection spectrum characterised by its location in the invisible or visible spectrum of light. The location in the spectrum may be unique to each image, such that the images are separable by wavelength-selective means and are therefore wavelength-multiplexed.

Brief Description of the Drawings

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Figure 1 shows an example of the multiple spectral peaks of a multiplexed reflection hologram, typical of those exhibited by a multiplexed holographic sensor.

Figure 2 shows another example of the multiple spectral peaks of a multiplexed reflection hologram typical of those exhibited by a multiplexed holographic sensor.

Figures 3a and 3b are each schematic drawings of a holographic sensor showing changing pictorial images.

Figures 4a to 4d are each schematic drawings of a holographic sensor illustrating a changing image in correspondence with the amount of substance detected.

Figure 5 is a schematic drawing of multiple features of a three-dimensional image.

Figures 6a to 6e are each schematic representations of a holographic sensor with changing numerical images.

Figures 7a to 7e are each schematic representations of a holographic sensor with calibrated numerical images.

Figures 8a to 8e are each schematic representations of a holographic sensor with changing alphabetical images.

Figures 9a and 9b are each schematic representations of a holographic sensor illustrating changing images in the form of messages relating to the application of the sensor.

Figures 10a to 10c are each schematic representations of a holographic sensor illustrating changing images in the form of messages relating to the amount of substance or substances being detected.

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Figure 11 is a schematic representation of a holographic sensor illustrating a changing image in the form of a moving indicator against a fixed scale.

Figure 12 is a schematic representation of a holographic sensor illustrating a changing image in the form of an indicator moving in the depth of the image against an image of a scale located in the depth of the image.

Figure 13 is a schematic of an optical layout which can be used to expose a photosensitive holographic film or plate to multiple images with the purpose of making a wavelength multiplexed holographic sensor.

Description of the Invention

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A sensor of the invention may be constructed and used in the manner generally described in WO-A-95/26499 or WO-A-99/63408. The contents of these publications, and other documents referred to herein, are incorporated by reference. Thus, for example, the matrix in which the holographic images are formed may be a chemically sensitive polymeric film, or it may comprise a plurality of films that are generally parallel (adjacent or separated by another type of layer). In such an arrangement, each film may provide its own dynamic range, and each film may be designed to detect or measure a specific substance. Each film may present one image or a sub-set of images with its own place in the dynamic range of the sensor; the dynamic range is created by having a plurality of films which provide a plurality or set of images.

More particularly, a sensor of the invention can be in the form of a polymer film or multiple films coated or otherwise disposed onto a transparent or opaque, flexible, semi-rigid or rigid substrate such as glass, plastic, paper or metal. The substrate can be printed, engraved or otherwise marked with a pattern or alpha-numerical markings so as to provide a reference to the holographic images.

The sensor can, alternatively, be provided in or onto a material which is component of or constitutes a device such as contact lens, spectacle lens, optical window into a reaction vessel, instrument display window, domestic window, visual display device or any component where an ambient substance is to be monitored or detected.

The sensor can, alternatively, be provided in or onto a material which is a component of or constitutes an item of clothing so as to confer the ability to monitor or detect ambient substances or physiological substances related to the wearer of the clothing.

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The invention can be in the form of multiple layers of holographic polymer films which are interleaved with other types of layers acting as transport media for substances to be detected or monitored or other components of a sample.

Illumination of the hologram(s) by ambient artificial or natural light can be directly onto the plane surfaces or, alternatively, can be provided by illuminating the polymer films along their edges, where the holograms are commonly known as "edge-lit" holograms.

A polymer film which is a sensitive element of the invention may be directly sensitive to an ambient substance or it may be sensitive to the product of a reaction or interaction between the ambient substance and one or more other ambient substances or substances which are provided specifically as components of the holographic sensor assembly. Such a film may be described herein as chemically sensitive, but this is for the purpose of illustration only.

Any of a variety of substances or analytes may be detected by means of the invention, including but not limited to those discussed in the prior art; reference herein to "a substance" includes the use of two or more such substances. Examples of analytes are water, organic liquids, ions, haptens, nucleotides, cells, aldehydes, enzymes, proteins, gases, metabolites, viruses, bacteria, fungi and yeasts. The analyte or a carrier medium may interact with the holographic matrix. In particular examples, the analyte is in liquid, e.g. an enzyme or ethanol in water, or water in an organic solvent.

In a preferred embodiment of the invention, each image from the set of the pictorial images that can be viewed depicts subject matter which is relevant to the sensor application. Each image may depict subject matter which is relevant to the response status indicated by the sensor.

The image may change from one picture to another in relation to the concentration of one or more substances to be detected by the sensor. The change in the pictorial image may be restricted to one or more parts of the image. A change in the pictorial image which is restricted to part of the image may be due to a response to a specific substance to be detected, such that a change in another part of the image is due to a response to another specific substance to be detected. Each part of the image which may be changed may be located anywhere in the three dimensions of the holographic image.

In another preferred embodiment of the invention, the set of images shows a sequence of numerical information which appears in a sequence corresponding to the

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concentration of one or more substances detected by the sensor. Preferably, the response of the sensor is calibrated so that the numerical images show numerical quantities which correspond directly with the concentration of a substance detected by the sensor.

In another preferred embodiment of the invention, the set of images shows a sequence of alphabetical information which appears in a sequence corresponding to the concentration of a substance detected by the sensor. Preferably, the alphabetical information is in the form of messages which are relevant to the sensor application. The response of the sensor may be calibrated so that the alphabetical information is in the form of messages which correspond directly with the concentration of a substance detected by the sensor.

In another preferred embodiment of the invention, each image of the set of images comprises an indicating feature which has a specific location, in the space of the image, corresponding to the concentration of a substance detected by the sensor. This is an example of a virtual instrument.

Preferably, the image or indicating feature is a shape. Alternatively, the indicating feature is a picture or is alpha-numerical.

The spatial degree of freedom of the location of the indicating feature may be parallel to the plane of the polymer film. Alternatively, the spatial degree of freedom of the location of the indicating feature is not parallel to the plane of the polymer film but is, instead, in the depth of the image which is an optional characteristic of a holographic image.

Preferably, the location of the indicating feature in either case is marked with reference to a visible scale. The visible scale may be provided as a holographic image provided by a hologram recorded in the same polymer layer as that which provides the indicating feature. Alternatively, the visible scale may be created by a holographic image provided by a different polymer layer from that which provides the indicating feature.

The visible scale may be incorporated with the polymer layer by photographic means. Alternatively, the visible scale may be printed onto the surface of the holographic element, or it may be printed onto a surface which is located adjacent to but separate from the holographic element.

Preferably, the visible scale which is provided as a holographic image is invariant with the concentration of the substance detected by the sensor.

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A holographic sensor can provide any combination of pictorial, alphabetical, numerical or spatially-indicating means of displaying the holographic response. Further, an array of holographic sensors may be provided, each providing any combination of the above pictorial, alphabetical, numerical or spatially-indicating means of displaying the holographic response to a multiplicity of substances to be detected or multiplicity of groups of substances to be detected.

Preferably, each element of an array of holographic sensors has a unique response characteristic to the substances to be detected.

The visible display provided by an array of holographic sensors may present an overall pattern which corresponds to the relative concentrations of substances to be detected. The pattern displayed by an array of holographic sensors may be pictorial, numerical or alphabetical. An alphabetical pattern displayed by an array of holographic sensors may represent a message which is relevant to the relative concentrations of substances to be detected.

In any of the above cases, the discrimination of any one visible image from its neighbours in a set of images presented by the holographic sensor can be provided by creating a significant separation in the peak reflected wavelength provided by each image from that of its neighbours.

The discrimination of any one visible image from its neighbours in a sequence of images presented by the holographic sensor may be improved by providing a colour transmission filter located between the light source and a chemically-sensitive polymer film containing the holographic recordings, or between the eye used to view the holographic image and the film, or immediately adjacent to the film but between the film and the eye.

The colour transmission filter may be an integral feature of the material to which a chemically-sensitive polymer film is attached. Alternatively, the colour transmission filter may be an integral feature of the chemically-sensitive polymer film. In any of the above holographic sensors, a colour transmission filter increases the number of multiplexed images for any given dynamic range of response of the sensor, by permitting each image to be closer in peak wavelength to that of its immediate spectral neighbour.

According to a further aspect of the present invention, a method for creating a holographic sensor which has a multiplicity of wavelength-multiplexed images of one or more types chosen from pictorial, numerical, alphabetical, spatially-variant or array types, comprises exposing a polymer film, having already been photosensitised, to a

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sequence of holographic exposures over the course of a transition of the film from one state of swelling to another.

Each image of the set of images has a characteristic reflection spectrum which may have a peak wavelength which is different from that of other images in the set.

By way of example, the initial state of swelling may be set by placing the polymer film, before exposure, in a solution having a specific pH or ionic strength. Then the polymer film is immersed in a solution with a different specific pH or ionic strength, respectively, so that the film undergoes a transition of swelling or contraction, depending on its response.

Alternatively, the initial state of swelling is set by placing the polymer film, before exposure, in an immediate environment having a specific relative humidity. Then the relative humidity is altered so that the film undergoes a transition of swelling or contraction, depending on its response to relative humidity.

An alternative method for creating a holographic sensor which has a multiplicity of wavelength-multiplexed images of one or more types chosen from pictorial, numerical, alphabetical, spatially-variant or array types is to expose the photosensitive polymer film to each image so that the angle between the object and reference beams used to create the holographic recording is unique to that particular image.

A preferred method for exposing the photosensitive polymer film to a set of images is to expose it to a timed sequence of images of a transmission object where the transmission object is an optical device which is commonly known as a spatial light modulator and is controlled by an electronic signal source, e.g. a computer or a video camera. Preferably, the form of the object represented by the spatial light modulator is chosen from pictorial, numerical, alphabetical, spatially-variant or array types.

Preferably, the image provided by the spatial light modulator is controlled so as to have variable spatial features during the transition of swelling or contraction, so as to provide a means of providing a holographic sensor which has a spatially-variant response to a range of concentrations of a substance to be detected.

The present invention will now be described by way of example only with reference to the accompanying drawings. These drawings illustrate the changing display of two or more holographic images in response to a substance or group of substances to be detected by a holographic sensor.

In any form of the invention, there exist two or more reflected holographic images, each with a colour characterised by a narrow band spectrum having a peak wavelength. A peak wavelength arises from constructive interference between

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components of light reflected and diffracted from a periodic structure such as a holographic structure which is composed of a periodic distribution of complex refractive index contained within a thin film of holographic material which is commonly a polymer or similar matrix. In holography, such a periodic distribution of refractive index is commonly known as a distribution of fringes. The peak wavelength is defined mathematically by the Bragg equation which is

$$\lambda_{\text{ok}}\{x,y,z\} = 2.n\{x,y,z\}.\Lambda\{x,y,z\}.\cos(\theta\{x,y,z\})$$

where n is an average index of refraction of the polymer film at a particular location defined generally by the co-ordinates x, y and z in the film, Λ is the local spacing between adjacent fringes and θ is the angle of illumination of light which is incident on the fringes at that location in the film.

Figure 1 shows a reflected intensity spectrum with a wavelength axis 4 showing three spectral peaks 1, 2 and 3 at one particular state in the dynamic range of the sensor. At this state, the only visible image is that characterised by the peak 2, situated in the region 5 of the spectrum which is normally visible to the eye, bordered by the ultra-violet end of the spectrum 6 and by the infra-red end of the spectrum 7. If the polymer film in which the sensor hologram is made swells during operation of the sensor then the characteristic peak wavelengths of the peaks 1, 2 and 3 all shift to longer wavelengths such that the image characterised by peak 1 originally invisible in the ultra-violet end of the spectrum becomes visible in a new spectral location 8. Similarly, the previously visible image characterised by the spectral peak 2 becomes invisible in the infra-red part of the spectrum, at a spectral location 9. Similarly, a response of the holographic sensor which is a contraction of the polymer film in which the sensor hologram is made is characterised by a shift of the peaks 1, 2 and 3 to shorter wavelengths.

In an alternative form of the invention, more spectral peaks per region of the spectrum can be provided whilst maintaining discrimination between adjacent images. Figure 2 shows a restriction of the region 5 of the spectrum which is available to be seen by eye or other detector to a narrower region 11 bounded by a lower end 30 set in this example by a long-wavelength pass filter and an upper end 7 at the upper end of the normally visible part of the spectrum 5. In general, a means of restricting the visible spectrum is not confined to a long wavelength pass edge filter but can be

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chosen from long wavelength pass filter, short wavelength pass filter, band-pass filter or any other optical device which restricts the detectable part of the whole spectrum. Figure 2 shows a reflected intensity spectrum with a wavelength axis 4 showing four spectral peaks 1, 2, 13 and 14 at one particular state in the dynamic range of the sensor. At this state, the only visible image is that characterised by the peak 2, situated in the narrower region 11 of the spectrum which is visible to the eye. If the polymer film in which the sensor hologram is made swells during operation of the sensor then the characteristic peak wavelengths of the peaks 1, 2, 13 and 14 all shift to longer wavelengths such that the image characterised by peak 13 originally invisible in the ultra-violet end of the spectrum becomes visible in a new spectral location 16. As the new image characterised by the spectral peak 16 appears the original visible image characterised by the spectral peak 2 becomes invisible as it moves to a new spectral location 17. As further swelling occurs the image characterised by the peak 1 becomes visible in the spectral location 16, or some such similar location in the confined visible region 11. One purpose of providing more spectral peaks per region of the spectrum is to allow a visible change in image to occur in response to a small swelling or contraction of the polymer film in which the holographic images are recorded. Another purpose of providing more spectral peaks per region of the spectrum is to provide a greater number of images throughout the dynamic range of the holographic sensor.

A preferred form of the invention is illustrated in Figure 3a which shows a schematic representing a holographic image 31 of a car provided by a holographic recording in a piece of holographic material 30. In this particular example, the car represents a purpose for which a holographic sensor may be designed, that of detecting the excessive presence of alcohol in the breath of an individual person. One way in which the device represented in Figure 3a may be used is to have a previously invisible image which becomes visible when saturated with moisture from the breath. In another way of using the device, the image such as that illustrated 31, could be always visible if provided in a state of saturation. The detection of excess alcohol in the breath is indicated by the change of the image 31 in Figure 3a to another image 32 in Figure 3b where the image illustrates pictorially that the tested person should not drive. The illustrations are given by way of example only and do not preclude the use of other pictorial images to convey other messages and instructions for the purpose of the use described or for any other application which uses pictorial information to illustrate the relative response of the sensor before and after use.

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Another preferred form of the invention is illustrated schematically in Figure 4a which shows a holographic material 30 providing, under illumination, an image of a shape 43 with a part 44 which is differentiated from the scale 43 by having a different appearance by way of colour, shape or pattern. The response of the sensor is indicated by the change in the image segment 44 to that 45 shown in figure 4b, illustrating an increase in the presence of a substance which is detected by the sensor by occupying a greater part of the image 43. Sequential response to greater amounts of a substance detected is indicated by progressive changes in parts 44 to 47 of the image 43, illustrated in Figures 4a to 4d. In this example, the spatial changes of the image or parts of the image are key features of this preferred form of the invention. An example of a particular application which utilises these essential features of the invention is as a medical diagnostic device which shows an image of a stylised form of the human body where a part of the image appears to be illuminated to indicate a biochemical, metabolic or pathological condition relating to the relevant part of the body.

Figure 4 illustrates a set of images where features of the images are located in a plane in space. The essential features of the invention are not limited to planar images but can, alternatively, be employed in three-dimensional holographic images. In another preferred form of the invention, the spatial changes of the holographic image or parts of the image are located in the three-dimensional space of the image. Figure 5 shows a sensor made in a holographic material 30 which provides an image in three dimensions indicated by the axes 54 in x, y and z and having features 51, 52 and 53. The features 51, 52 and 53 can be made to appear or disappear or change in appearance by way of colour, shape or pattern as the visible means of observing the operation of the sensor.

In any holographic sensor where an image or part of an image is made to change or become visible or invisible, the image or part of an image can have numerical form, as illustrated schematically in Figure 6a. Numerical images 60-65 shown in Figures 6a to 6e illustrate a response in relation to the concentration of a substance or group of substances to be detected by the sensor. Alternatively, the numerical response of a holographic sensor can be calibrated to the concentration of a substance or group of substances to be detected, as illustrated in Figures 7a to 7e, by images 71-75.

In any holographic sensor where an image or part of an image is made to change or become visible or invisible, the image or part of an image can have alphabetical form, as illustrated schematically in Figure 8a. Alphabetical images 81-85

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shown in Figures 8a to 8e illustrate a response in relation to the concentration of a substance or group of substances to be detected by the sensor.

In any holographic sensor, the images can optionally show a combination of numerical or alphabetical information relating to the application for which the sensor is intended.

In any holographic sensor which presents alphabetical information, the message which is provided can be related to the application for which the sensor is intended. An example of a holographic sensor for breath alcohol is illustrated in the schematic of Figure 9a which shows a message 91 indicating that the measured level is within bounds accepted by predetermined rules. The schematic of Figure 9b illustrates an example of a message 92 which indicates that the measured level falls outside bounds accepted by predetermined rules.

In any holographic sensor which provides alphabetical information, the message which is provided can be related to the concentration of substance or group of substances to be measured. Figure 10a shows an alphabetical image 101 which indicates a low detected level of substance or group of substances. Figures 10b and 10c indicate, respectively, normal and high levels, by images 102 and 103. Alternatively, the messages provided can be an indicator as to the course of action to be followed as a consequence of carrying out the test provided by the holographic sensor.

The presentation of simple messages in the fashion provided by holographic sensor devices provides an unambiguous and easily understood result and is particularly suitable for rapid tests or use by unskilled people in a variety of healthcare, consumer or clinical applications though other applications areas are included.

In another preferred form of the invention, illustrated schematically in Figure 11, each of the multiplexed holographic images is in the form of a pointing indicator. A series of such indicators is multiplexed according to methods described above such that, preferably, only one is visible at any one response state of the sensor. In the example shown in Figure 11, just two of the indicator images 112 and 113 are shown, though a series of images separated spatially along the direction 114 provides a sequence related to the concentration of a substance or group of substances to be quantified. The pointing indicators 112 and 114 and others not shown in the diagram refer to a scale 111 which can be pictorial or numerical. A numerical scale 111 provides a means of quantifying the response of the sensor. The scale 111 can be chosen from the following types: printed adjacent to the holographic material, printed onto the

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holographic material, printed on a separate material under the holographic material, photographically created separate to the holographic material, photographically created within the holographic material, holographically created within the holographic material, holographically created in a separate holographic material from that which serves as the sensor material, though the list is not exclusive.

In another preferred form of the invention, illustrated schematically in Figure 12, each of the multiplexed images is in the form of a pointing indicator which appear to be arranged in three dimensions, out of the plane of the holographic material 30. The characteristic depth which is optionally provided by holographic images is utilised in this form of holographic sensor. A series of such indicators is multiplexed according to methods described above such that, preferably, only one is visible at any one response state of the sensor. In the example shown in Figure 12, just two of the indicator images 122 and 123 are shown, though a series of images separated spatially along the direction 124 in three spatial dimensions provides a sequence related to the concentration of a substance or group of substances to be quantified. The pointing indicators 122 and 124 and others (not shown) refer to a scale 121 which can be pictorial or numerical. A numerical scale 121 provides a means of quantifying the response of the sensor. The scale 121 is preferably itself a holographic image which is aligned with the sequence of multiplexed pointing indicator images though it can be chosen from the following types: printed onto the holographic material, printed on a separate material under the holographic material, photographically created separate to the holographic material, photographically created within the holographic material, holographically created within the holographic material, holographically created in a separate holographic material from that which serves as the sensor material, though the list is not exclusive. Some benefits of using three-dimensional holographic images in a holographic sensor are that the area of the holographic material can be reduced, allowing test sample volumes to be reduced, manufacturing cost to be reduced and space to be saved.

A preferred method for constructing the multiplexed images for the purpose of providing a holographic sensor is to use a two-beam image-hologram process such as that illustrated by way of example in the schematic of Figure 13. A laser beam 131 is split into two beams 132 and 133 by a beam-splitter 134. One of the beams 132 is directed by a mirror 135 onto a transparent object 136 via an optional light diffuser 140. Preferably, the transparent object 136 is a spatial light modulator which is a video display device which provides an image under computer control. Alternatively, the

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transparent object 136 can be a photographic transparency. A benefit of using a computer-controlled spatial light modulator is that the transparent objects it provides as images to be recorded holographically can be rapidly changed in order to create the sequence of holographic images. The illuminated transparent object 136 is located at the object plane of an imaging system 137 which is a set of one or more lenses which provides an image of the object 136 at an image plane where a holographic recording material 138 is situated. The second laser beam 133 is directed, in this example, by a mirror 139 onto the holographic recording material 138 and thus acts as a reference beam (in holographic terminology). The image and the reference beams combine to produce an interference pattern in the holographic recording material 138 in such a way as to allow it to be retained by the material. Two examples of methods of recording a holographic interference pattern are by further chemical processing, if a silver-based recording material, or by using a photo-polymer material and appropriate laser wavelength. An essential feature of this aspect of the invention is that the state of swelling of the holographic recording material 138 is controllable by some means chosen from pH, ion concentration, humidity, water activity or any other means of altering the thickness of the holographic recording material. At each state of swelling of the material a different holographic image is created by the means described until a complete set has been recorded as a set of multiplexed images which display the response of a holographic sensor in the formats described above.

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CLAIMS

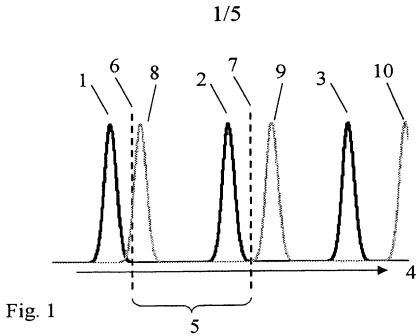
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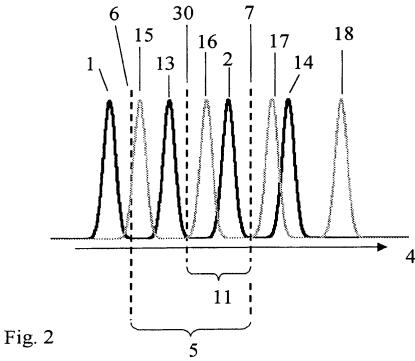
- 1. A holographic sensor which comprises a thin film polymer matrix that undergoes a change in response to a substance to be sensed, the matrix containing within its volume a set of two or more holographic recordings, each recording providing a holographic image when the sensor is illuminated, wherein the presence or appearance of each image is visible to the eye as a function of the response of the sensor to the substance to be sensed, and the images provide the dynamic range of the sensor.
- 2. A sensor according to claim 1, wherein each image has a unique location in the visible or invisible spectrum.
- 10 3. A sensor according to claim 1 or claim 2, wherein each image is pictorial, numerical and/or alphabetical.
 - 4. A sensor according to any preceding claim, which provides a visible image in the presence of the substance.
- 5. A sensor according to claim 4, wherein the visible image is representative of the substance or a scenario in which the substance is found or the sensor is used.
 - A sensor according to claim 5, wherein the visible image is numerical.
 - 7. A sensor according to claim 5, wherein the visible image is alphabetical and provides a message corresponding to the substance or a scenario in which the substance is found or the sensor is used.
- 20 8. A sensor according to claim 5, wherein the visible image has a location, in the space of the image, corresponding to or representative of the substance or a scenario in which the substance is found or the sensor is used.
 - 9. A sensor according to any of claims 4 to 8, wherein the visible image is calibrated with respect to the quantity of the substance.
- 25 10. A sensor according to any of claims 4 to 9, which provides another visible image in the absence of the substance.
 - 11. A sensor according to any preceding claim, which additionally comprises a visible scale.
- 12. A sensor according to claim 11, wherein the scale is invariant with respect to the concentration of the substance.
 - 13. A sensor according to any preceding claim, which provides multiple images within one film.
 - 14. A sensor according to any preceding claim, which provides at least three images.

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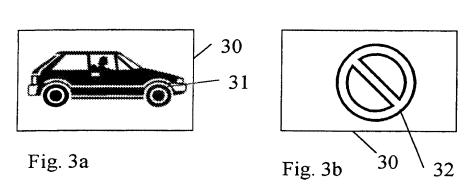
- 15. A sensor according to any preceding claim, which comprises a plurality of films each providing its own dynamic range within the dynamic range of the sensor.
- 16. A sensor according to any preceding claim, which comprises a plurality of films each responding to a different substance.
- 5 17. A sensor according to any preceding claim, which additionally comprises a colour transmission filter.
 - 18. A sensor according to any preceding claim, where the image is formed from a set of visible pixels, the pattern of pixels being indicative or representative of the substance or a scenario in which the substance is found or the sensor is used.
- 10 19. Apparatus comprising a sensor according to any preceding claim and an illumination source.

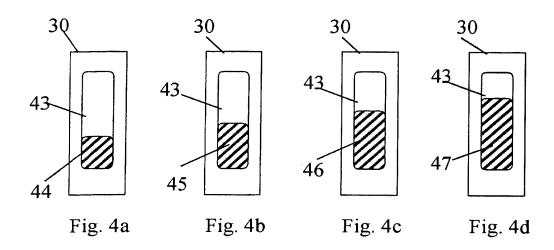
PCT/GB01/00061 WO 01/50113

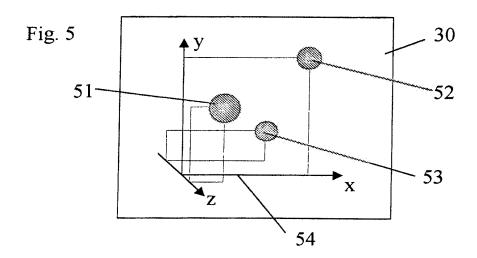




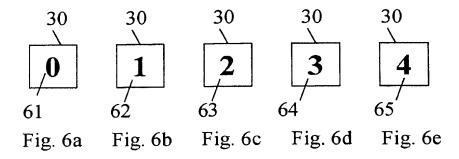


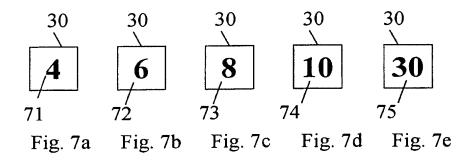


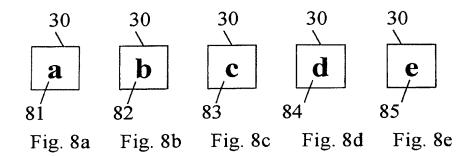




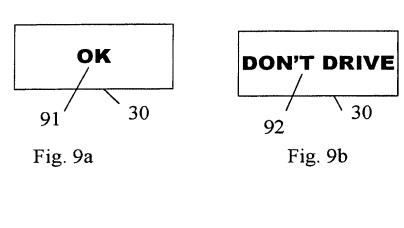
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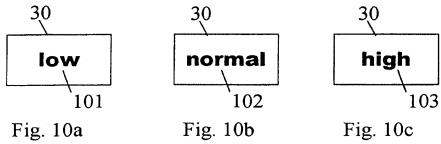


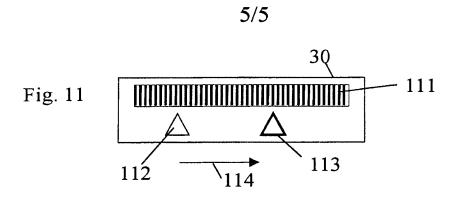


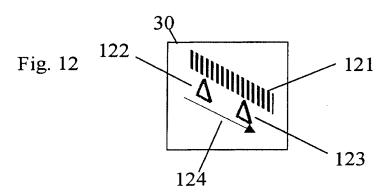


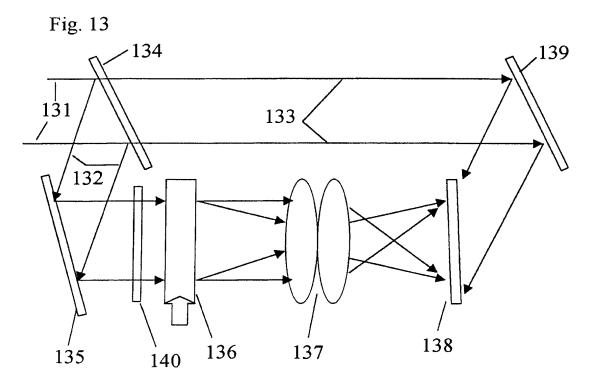
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INTERNATIONAL SEARCH REPORT

Inter. nal Application No PCT/GB 01/00061

A. CLA	ASSIFIC	ATION OF	SUBJECT	MATTER	
IPC	7	G01N21	L/75	G03H1	/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 G01N G03H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Υ	WO 99 63408 A (MAYES ANDREW GEOFFREY; UNIV CAMBRIDGE TECH (GB); BLYTH JEFFREY (GB) 9 December 1999 (1999-12-09) cited in the application page 3, line 20 -page 4, line 19 claims 1,12	1		
Υ	WO 95 26499 A (BRITISH TECH GROUP; LOWE CHRISTOPHER ROBIN (GB); MILLINGTON ROGER) 5 October 1995 (1995-10-05) cited in the application page 3, line 20 -page 5, line 5 page 10, line 15 -page 11, line 5 claims 1,5,9	1		

Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
20 March 2001	29/03/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2	Authorized officer
NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Krametz, E

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INTERNATIONAL SEARCH REPORT

Interi nal Application No
PCT/GB 01/00061

		PC1/GB 01/00061
C.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 43086 A (KIMBERLY CLARK CO) 1 October 1998 (1998-10-01) page 5, line 12 - line 28 page 10, line 12 -page 11, line 2 page 26, line 3 - line 11 claims 1,2,22	1
A	US 5 611 998 A (AUSSENEGG FRANZ ET AL) 18 March 1997 (1997-03-18) column 1, line 35 - line 58 claim 1	

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter: nal Application No
PCT/GB 01/00061

Patent document cited in search repor	-t	Publication date		Patent family member(s)	Publication date
WO 9963408	Α	09-12-1999	AU EP	4051099 A 1082643 A	20-12-1999 14-03-2001
WO 9526499	A	05-10-1995	AU CA EP GB US	2076795 A 2186603 A 0753139 A 2301886 A, 5989923 A	17-10-1995 05-10-1995 15-01-1997 B 18-12-1996 23-11-1999
W0 9843086	Α	01-10-1998	AU	6763898 A	20-10-1998
US 5611998	Α	18-03-1997	AT AT DE EP	403746 B 75394 A 59508548 D 0677738 A	25-05-1998 15-09-1997 17-08-2000 18-10-1995